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NO_2 MEASURING SYSTEM

AEROSPACE CORPORATION

PREPARED FOR
ENVIRONMENTAL PROTECTION AGENCY

MAY 1974

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A Laser NO_2 Monitor Prototype developed for the EPA is described. The detectability of the instrument was 0.6 ppbv for an 80 sec integration time. The response of the instrument was found to be linear over the range tested, 10 to 1000 ppbv. Measurements of the ambient NO_2 levels in the atmosphere in the vicinity of our laboratory showed a highly satisfactory performance of the instrument.

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FINAL REPORT

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NO_2 MEASURING SYSTEM

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I. PURPOSE AND SCOPE OF PROGRAM

The purpose of this program is to develop a prototype "NO_2 Measuring System" based upon a method originated at The Aerospace Corporation. A laser is used to excite the NO_2 molecules, whose concentration in the atmosphere is monitored by their resultant fluorescence. The method is of great sensitivity, i.e., 1 ppbv can be readily detected. The signal is obtained from the NO_2 molecules and therefore the method does not involve chemical processing or other procedures which could compromise the accuracy of the measurements. The technique has been found to be free of interference due to the presence of other gases. The fluorescence methods can provide real-time, automatic monitoring of ambient atmosphere NO_2 levels. In short, the prototype "NO_2 Measuring System" can provide the EPA with a unique means of monitoring ambient NO_2 levels.

II. OUTLINE OF TASKS

The plan outline of work under EPA Contract No. 68-02-1255, "NO_2 Measuring System" consisted of the following: (1) procurement of major components, (2) design and (3) assembly of the electronics which was tested with the Aerospace NO_2 measurement system, (4) packaging of the NO_2 measurement system, (5) calibration and (6) system performance tests as specified in the EPA contract.

In the main, the prototype is similar to the systems operated at the Aerospace Corporation. Two important features incorporated into the system for the EPA are: a He-Cd cw laser operating at 442 nm used to excite the NO_2 fluorescence and (2) the fluorescence chamber redesigned for improved performance.

The cw He-Cd laser is a compact instrument of approximately 10 mW output at 442 nm. Its virtues, compared to the cw argon ion laser used in prior work at Aerospace [1,2] are its compactness and relatively lower cost. The output power of the He-Cd laser (10 mW) is a factor of 100 less than that of the cw 488 nm argon ion laser output. The utilization of the He-Cd laser did, of course, require careful design to obtain the required performance accuracy.

III. CHARACTERISTICS OF THE LNMP (LASER NO_2 MONITOR PROTOTYPE)

1. Description

The appearance of the LNMP may be inferred from the photographs reproduced in Figures 1 to 4. The arrangement of the components is clearly visible in Figures 2 and 3 which show respectively the front view (with cover panels removed) and the back view (with rear access doors open). For ease in operation, adjustment and servicing, the Laser NO_2 Monitor is configured of two subsystems (1) an optical assembly and (2) the electronics and data recording system. The optical subsystem assembly is easily identified by the He-Cd laser (Figure 2) and the chamber and photomultiplier tube housing (Figure 3). A cooled photomultiplier tube in conjunction with a photon counting system is used to detect the weak fluorescence. The relevant spectroscopic properties of NO_2 in absorption and fluorescence have been described in earlier reports.[1, 2]

2. Optical Subsystem

The heart of the LNMP lies in the optical subsystem shown in the photograph of Figure 5 and the block diagram of Figure 6. The Liconix Model 401 He-Cd laser emitting at 442 nm with a nominal output of 10 mW is used for excitation.

A major technical problem in the design of a sensitive LNMP is that of background signals. It is found that most materials emit a broad-band red fluorescence when excited by visible light. Thus, scattered laser light striking components of the chamber results in a broad-band fluorescence. This signal is observed when the laser beam is introduced into the evacuated chamber (pressures less 10 mtorr) and when the chamber is filled with pure gases (such as He, N_2, etc) which (as far as is known) do not contain fluorescing species. This signal, we refer to as background. A development of an instrument with a low background signal is the key to the attainment of high sensitivity. Many of the details of the optical arrangement described below are used to maximize the NO_2 fluorescence while minimizing the background.

In the LNMP developed for the EPA, key features which have resulted in high sensitivity, low background and ease of operation are: (1) development of an almost optimal fluorescence band-pass filter in conjunction with excitation at 442 nm and (2) the liquid filter cells (Nos. 1 and 2 of Figure 6) which reduce background signals.

The layout of the laser and chamber, shown in Figure 6, is dictated in part by requirements of compactness and low background signals. Practially all components which appear between the laser output end and the chamber end have been selected with a view to minimize the background. These are: (1) A Corning Glass Filter No. CS-5-61 to absorb the red end-light emitted by the laser while transmitting the 442 nm laser light; (2) 442nm mirrors which have high reflectivity at 442nm and low reflectivity at longer wavelengths, particularly in the orange-red spectral band; (3) aperture and lens to reduce scattered laser light and improve laser beam collimation. This reduces the background signal and permits utilization of a small aperture (1.8 mm dia.) just behind the entrance Brewster angle window. It should be noted that the LNMP operates without a noticeable increase in background at low ambient light levels. This desirable feature has been achieved with the combination of lens and baffles (particularly the two baffles just behind the entrance Brewster angle-window). The features described above which function primarily to reduce background cannot be considered an invariable feature of the LNMP. We have operated satisfactorily a breadboard model in our laboratory without the lens and baffles of Figure 6.

The design of the chamber (Figures 5 and 6) for the LNMP is a practical implementation of a working design and should not necessarily be considered optimal. Most of the components within the chamber have been configured to minimize the background signal. The entrance and exit windows are fabricated of fused silica (low visible fluorescence) and are carefully polished to minimize scattering of laser light. In the

arrangement of Figure 6, a unique feature of the LNMP is the specially designed liquid filters.

Filter section 2 (the center section) is filled with an aqueous solution of $Na_2 Cr_2 O_7 . 2H_2O$ (304 g/l). This solution strongly absorbs the scattered 442 nm laser light without any detectable fluorescence and, in addition, strongly absorbs the scattered Raman light due to O_2, N_2 and water vapor. When using 442 nm excitation, the water vapor line (furthest towards the red) occurs at 526 nm. The transmission characteristics of a $Na_2 Cr_2 O_7$ filter are shown in Figure 7 for a 304 g/l solution of 1 cm path length which is identical to the concentration and path length of filter section 2 (Figure 6). From Figure 7, it is evident that the 304 g/l $Na_2 Cr_2 O_7$ solution of 1 cm path begins transmitting at 550 nm and sharply rises to 90% transmission at 600 nm. The absorption coefficient of this filter at 442 nm is, $k = 1034\ cm^{-1}$. The absorption coefficient is defined by: $I_t = I_o e^{-kL}$ (Beer's Law). A Corning glass filter No. CS 3-66 (low wavelength cutoff at 555 nm) was placed in front of the PMT to provide additional attenuation at the Raman line of water vapor (526 nm).

In the two filter sections (1, Figure 6), a solution of 600 g/l $CoSO_4$ and a 600 g/l $NiSO_4$ solution was used. This was found to result in fewer background counts than that obtained with a 312 g/l solution of $Na_2 Cr_2 O_7 . 2H_2O$.

The cells containing the solutions were fabricated of fused silica. Fused silica is preferable to pyrex glass because its broad-band red fluorescence is much weaker than that of the pyrex glass. The inner diameter of the filter cells was approximately 2 cm.

Six baffles (shown in Figure 6) were used to reduce scattered laser light and, thereby, resulted in lowering the background signal. The two baffles just behind the front Brewster window provided the greatest reduction in the background.

The final element in the chamber is the beam absorber, designed to absorb the laser beam with a minimal increase in background. This is accomplished with a liquid filter cell with a fused silica Brewster angle entrance window filled with the 304 g/l sodium dichromate solution. It is obvious that improved sensitivity could be obtained by utilizing a mirror to reflect the laser light back along the same path and increasing the path length over which the fluorescence is observed.

A simple means of increasing the sensitivity was employed and consisted of a cylindrical front surface aluminized mirror on a fused silica substrate placed around the rear of the center section filter to reflect fluorescence light into the PMT. This resulted in a signal increase by a factor of about 1.5 and a small increase in the background

3. Electronics Subsystem

The fluorescence is monitored by a cooled PMT (EMI 9659 QAM) followed by a wide band amplifier and a high speed electronic counter to count the electrical pulses produced by light impinging on the photocathode. An RF shielded PMT refrigerator chamber minimizes interference from external sources of RF radiation. The PMT is operated in a grounded cathode configuration with the cathode attached to the RF shield. The PMT is cooled to -25^{o}C to reduce the number of dark current pulses. Under separate cover, a full set of the manufacturer's instruction booklets and detailed circuit diagrams of each component has been delivered to EPA personnel together with the LNMP at Research Triangle Park, North Carolina. A detailed circuit diagram of an integrator which is incorporated into the LNMP designed by the Aerospace Corporation is part of the detailed description of the unit. In addition, a very detailed set of instructions for operation and adjustment of the instrument has been included with the operating manuals. Thus in this report only a brief description of the LNMP electronics will be included.

The output pulses of the cooled PMT are fed to a wide band, high gain amplifier/discriminator (SSR Model # 1120). The output of this amplifier consists of pulses of standard 25 nsec width and -1.5V amplitude and are fed to a 100 MHz counter (Newport Labs, Model # 700). A clock and printer, together with the required storage circuit are provided to secure several types of operation. In the repetitive timed mode of operation, the counter records the number of counts in a preset interval (10 sec, 100 sec, and etc.), determined by the internal time base of the counter. At the end of this period, this information is transferred to a storage circuit. The counter is automatically reset and begins recording counts for the next consecutive period. The counter dead time during the resetting is about 0.1 sec. The number of counts recorded is transferred to the dials of the print unit together with the date and time and is printed out on a 2-1/4 inch wide strip of paper.

The alternative mode of operation is provided by means of an electronic integrator. In the integrator mode, after a preset laser energy is measured (for example, 10 mW for 100 sec results in 1 J total output), the number of counts accumulated by the counter is transferred to the storage circuit then to the printer wheels of the printer unit and is printed out on paper tape together with the date and time. The advantage of the integrator mode of operation is that the signal counts recorded during the interval depend only on the total preset laser energy delivered to the sample and not on the instantaneous power levels during the interval. Thus, the results are independent of the power variations during the intervals.

For continuous monitoring, it is desirable that the data be processed by a computer. With simple modifications, the LNMP could be provided with an on-line computer which would process the data and provide a read-out of the concentration of NO_2 in the ambient atmosphere.

Photon counting is among the most sensitive methods of detection of low light level signals. The heart of the system is the PMT which provides approximately noiseless amplification of the photon signal. A photon that produces a photo-electron, is amplified and produces a pulse of current which signals this event. The current pulse exhibits, considerable variability in terms of amplitude, width, etc., but this does not prevent an unambigous recording of the release of a photo-electron.

The difficulty with the PMT resides in the existence of other processes which result in the release of an electron producing a current pulse indistinguishable from that generated by photons. Among these effects are dark current or thermionic emission from the photocathode, UV radiation produced by cosmic-ray induced Cerenkov pulses, other effects of cosmic rays and unidentified sources of radiation.[3,4,5] A selected EMI 9659 cooled to -25°C operates with about 45 c/sec (with the shutter closed).

After adjustment of the PMT high voltage to secure operation on the "plateau", it was hoped that the fluctuations in the counts could be described by Poisson statistics. Tests with a selected low dark current tube are summarized in Table I. A minimum detectable concentration is defined to be that for which the variation in the number of signal counts just equals the number of signal counts, namely, $S/\sigma = 1$, where S is the signal due to the NO_2 concentration, and σ is one standard deviation of the signal counts. According to the results shown in Table I, an operating detectability of 0.9 ppbv was obtained for a 100 sec integration time. Had the fluctuation exhibited a Poisson distribution, a detectability of 0.41 ppbv would have resulted. Other investigators have also noted departures from Poisson statistics and have tried to identify the causes.[3,4,5] Note that by increasing the integration time the detectability increases (as the square root of the integration time) and, in principle, very high sensitivites can be obtained by utilizing long integration periods. The presence of background counts at low NO_2 levels

reduces the sensitivity. For example, if the background counts had been eliminated, the detectability of the LNMP would be 0.09 ppbv a ten fold improvement over the value listed (0.9) for a 100 sec integration time.

IV. CALIBRATION AND SYSTEM PERFORMANCE

In this section, we will summarize many tests carried out to delineate the performance of the LNMP. All tests specified in the contract have been satisfactorily completed. The detectability of the LNMP is better by more than a factor of ten than the contract specification of 10 $\pm$ 5 ppbv (parts per billion per unit volume).

In prior work on a similar system, no interferences with NO_2 measurements had been detected as a result of the presence of other gases. In the present contract, tests were made for possible interference resulting from water vapor up to the saturation value. A vapor saturated air sample was prepared and directed through the chamber and did not result in a significant increase in the background counts. Therefore, we concluded that the presence of water vapor up to the saturation point did not show a detectable signal. The fact that water-vapor does not interfere with NO_2 measurements was already known from earlier tests.[1,2]

The tests involving calibration and linearity of the LNMP specified in the contract have been performed and have shown the LNMP calibrations to be highly reproducible. Within experimental error the response of the LNMP was shown to be linear over the range of 1 pphmv to 1 ppmv.

One of the tasks specified in the contract was the determination of the calibration constant of the unit for 10 consecutive days. The purpose of these tests was to demonstrate the repeatability and reliability of the LNMP. A summary listing of the measurements performed on 11 consecutive working days is shown in Table II. The uncertainty in the calibration constant is due to the statistical fluctuation of the background and signal counts and mostly due to the uncertainty of the known NO_2 sample ($\pm$ 2.5%). However, 73% of the values fall within 1 standard deviation of the mean. We consider the minimum detectability (D) of the

system to be $\sqrt{2}$ times the standard deviation (σ) of the background counts divided by the calibration constant(C), ($D = 1.4\sigma/C$). For example, in the case of the first entry, the instrument detectability was 0.59 ppbv. Note that this refers to a background of 45706 $\pm$ 366 counts in an 80 sec integration time. Much greater sensitivity can be obtained by utilizing longer integration times. To provide some information on the measurements involved in a single determination of the calibration constant we list the values for the first entry: temperature, 23.62 $\pm$ 0.02°C; pressure, 760 $\pm$ 3 Torr; flow rate, 4.65 $\pm$ 9.14 liters/min.; permeation rate 0.939 μg/min. (manufacturer's calibration of 1.055 μg/min $\pm$ 2% at 25°C); NO_2 concentration of 10.68 $\pm$ .25 pphmv; background counts with N_2, 45706 $\pm$ 366; signal plus background counts 138690 $\pm$ 445; NO_2 signal counts, 92984 $\pm$ 576; calibration constant, 8706 $\pm$ 211 counts/pphmv. A standard error analysis following the method of ref (6), has been used in evaluating the measurement uncertainties and in combining them in order to obtain an overall estimated precision.

One of the most important operational parameters of the LNMP is that of linearity of response. This has been extensively checked and the results are shown in Figures 8 and 9. We have also demonstrated that the number of counts is proportional to the laser power for a constant concentration of NO_2. This data is shown in Figure 10.

Linearity tests over the range of 1 to 10 pphmv for filter and unfiltered samples are shown in Figure 8. The curves are linear within experimental error and establish that the presence of a filter in the sample path does not interfere with the linearity. The data over the concentration range of 10 to 100 pphmv is shown in Figure 9. The linearity of the LNMP is clearly evident and is not affected by insertion of an aerosol filter. We stress the fact that linearity of the LNMP was expected and this was borne out in the subsequent tests.

One effect of importance in the use of this instrument was noted in carrying out these tests. When using concentrations of NO_2 above

50 pphmv, the background levels begin to show a marked increase. This is apparently due to adsorption of NO_2 on the walls of the chamber and the connecting tubes. The background can be reduced to a low level by opening the chamber and cleaning. In normal use where concentrations seldom go above 10 pphmv, the system was observed to operate for long intervals without any increase in the background counting rate.

V. AMBIENT AIR NO_2 LEVELS AT LOCATION OF THE AEROSPACE CORPORATION

After completion of the calibration and linearity tests, the LNMP was used to monitor the ambient air in the vicinity of our building. The general geographical location is just southeast of Los Angeles International Airport near the intersection of Aviation and El Segundo Boulevards. The air sample was drawn into the lab through PVC tubing with an orifice 15 ft. above the roof of our building; the overall length of the piping to our chamber was approximately 40 ft. A flow rate of 4.5 liters/min. was used and the air sample was filtered to remove aerosols.

The data reduction was accomplished with our CDC 7600 computer and the computer generated curves showing the ambient levels of NO_2 are shown in Figures 11 - 13. A noteworthy feature is the low levels of NO_2 during a rainy period (Figure 11) and the higher levels with the return of the usual Los Angeles climatic pattern (Figures 12 and 13). The 28th and 29th of March were cloudy days. On the 30th of March, it rained and on this day (Figure 11) the lowest concentrations of NO_2 were observed.

CONCLUSIONS

The construction and operation of the Laser NO_2 Monitor Prototype, developed for the EPA under contract No. 68-02-1255, are described in this report. Several new features not present in earlier embodiments of the laser-induced NO_2 fluorescence monitor, were incorporated. A He-Cd laser was used for excitation. This provided an economical and compact excitation source. A new type of low fluorescence solution filter

was developed which resulted in greatly improved sensitivity. The LNMP was found to operate in a highly reproducible manner (Table II) and possessed a detectability almost a factor of 10 greater than specified by the contract. Saturated water vapor levels did not result in any detectable interference. The response of the instrument with respect to concentration of NO_2^- was found to be strictly linear over the range tested, 1.0 to 100 pphmv. Measurements of the ambient NO_2^- levels in the atmosphere in the vicinity of our laboratory building showed a highly satisfactory performance of the instrument.

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ABBREVIATIONS

Laser NO_2 Monitor Prototype	LNMP
parts per billion per unit volume	ppbv
parts per hundred million per unit volume	pphmv
parts per million per unit volume	ppmv
photomultiplier tube	PMT

LIST OF TABLES

I. Performance of Prototype.

II. Instrument Sensitivity - Consecutive Daily Calibrations (11 days).

TABLE I

PERFORMANCE OF PROTOTYPE

10mW at 441.6nm

$S/\sigma = 1$	Min. Det. Concentration (ppbv), D_m Integration Time	
	10 sec	100 sec
Poisson Statistics	1.3	0.4
Measured Values	2.9	0.9

S is the number of counts due to the NO_2 concentration.

σ is the standard deviation in S.

$D_m = \sigma / C$

C = calibration constant

TABLE II

INSTRUMENT SENSITIVITY

CONSECUTIVE DAILY CALIBRATIONS (11 DAYS)

Day in March 1974	NO_2 SIGNAL COUNTS for one pphmv	MINIMUM DETECTABLE CONCENTRATION 80 SEC INTEGRATION TIME (pphmv)
13	8706 ± 211	0.059
14	8430 ± 204	0.065
15	8732 ± 215	0.033
16	9274 ± 229	0.044
18	8720 ± 213	0.066
19	8379 ± 216	0.090
20	8289 ± 205	0.074
20	8870 ± 230	0.057
21	8780 ± 218	0.061
22	8835 ± 220	0.059
23	8846 ± 216	0.056

INSTRUMENT CAPABILITY

1 pphmv ± 0.06 pphmv

CONTRACT SPECIFICATION

1 pphmv ± 0.50 pphmv

LIST OF FIGURES

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12. Atmospheric NO_2 concentrations, El Segundo, California April 1-3, 1974.
13. Atmospheric NO_2 concentrations, El Segundo, California April 4 and 5, 1974.

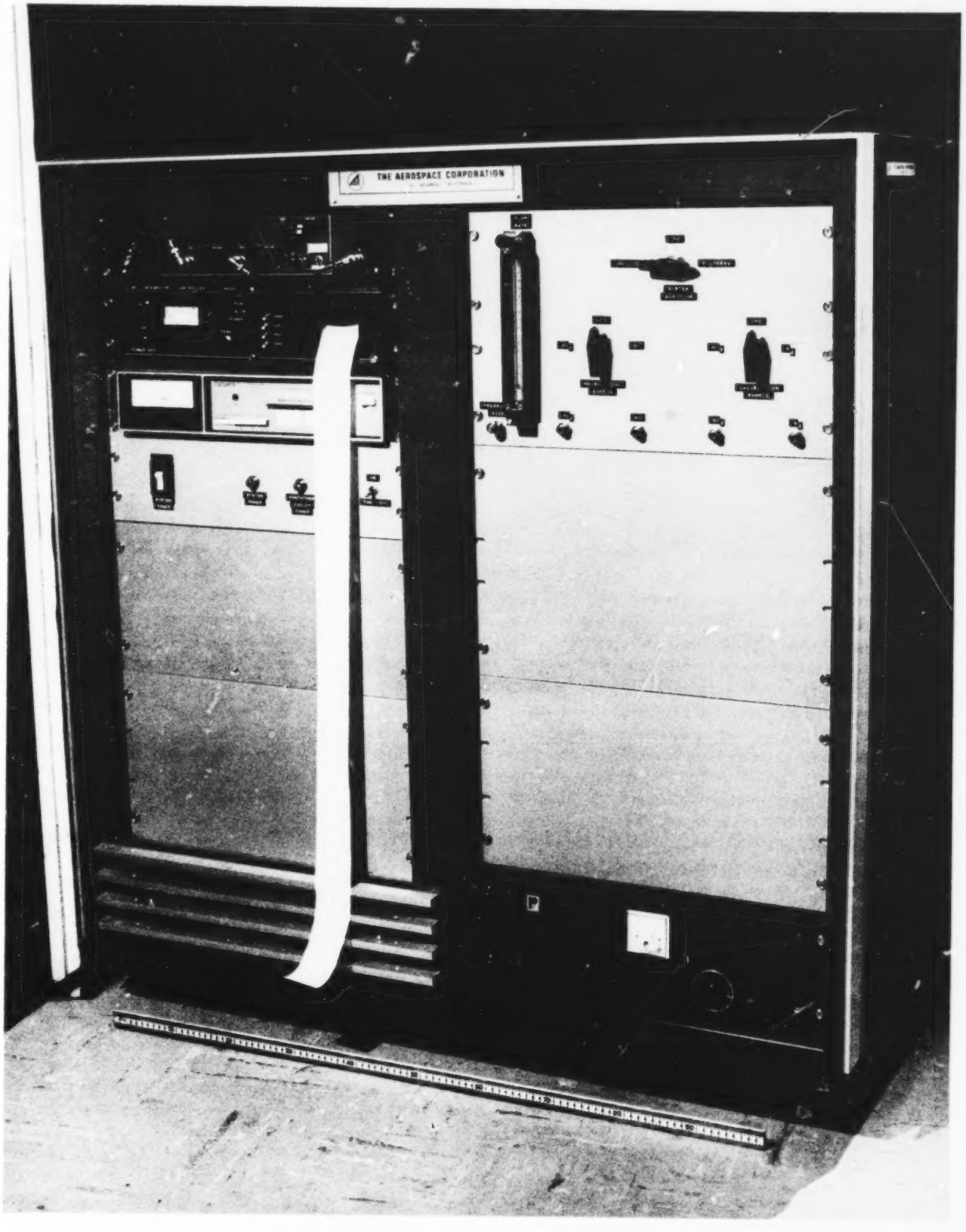


Figure 1, Page 19

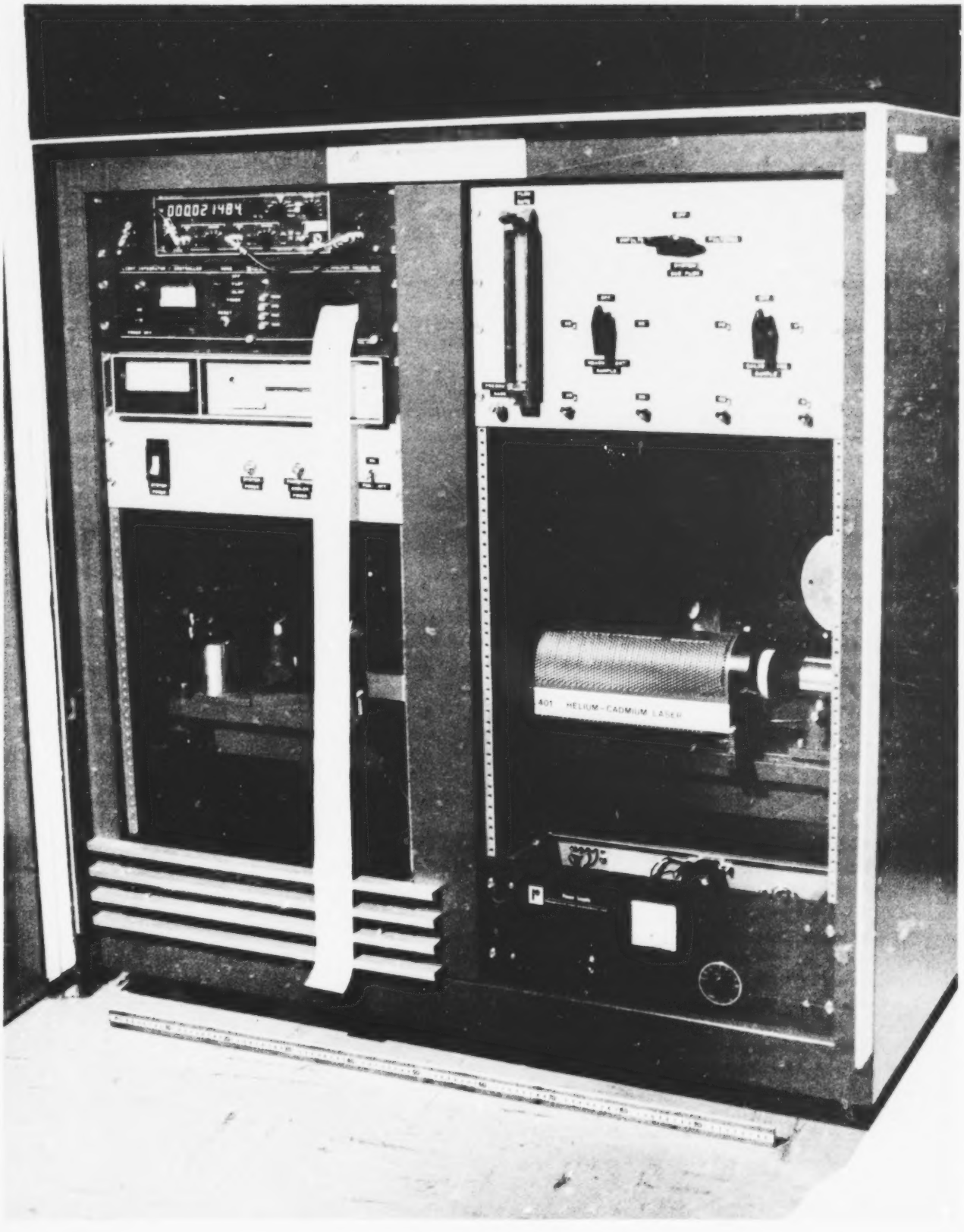


Figure 2, Page 20

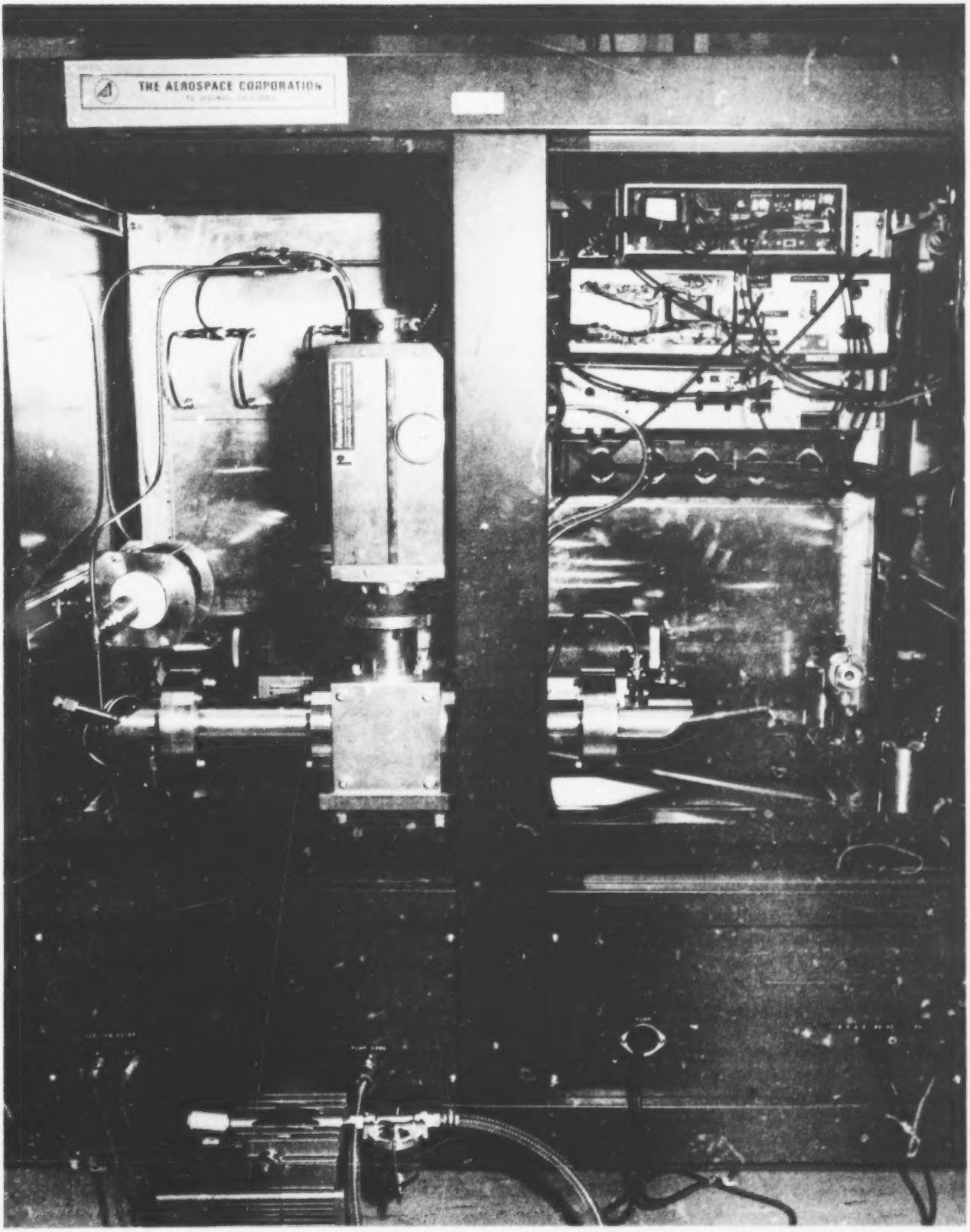
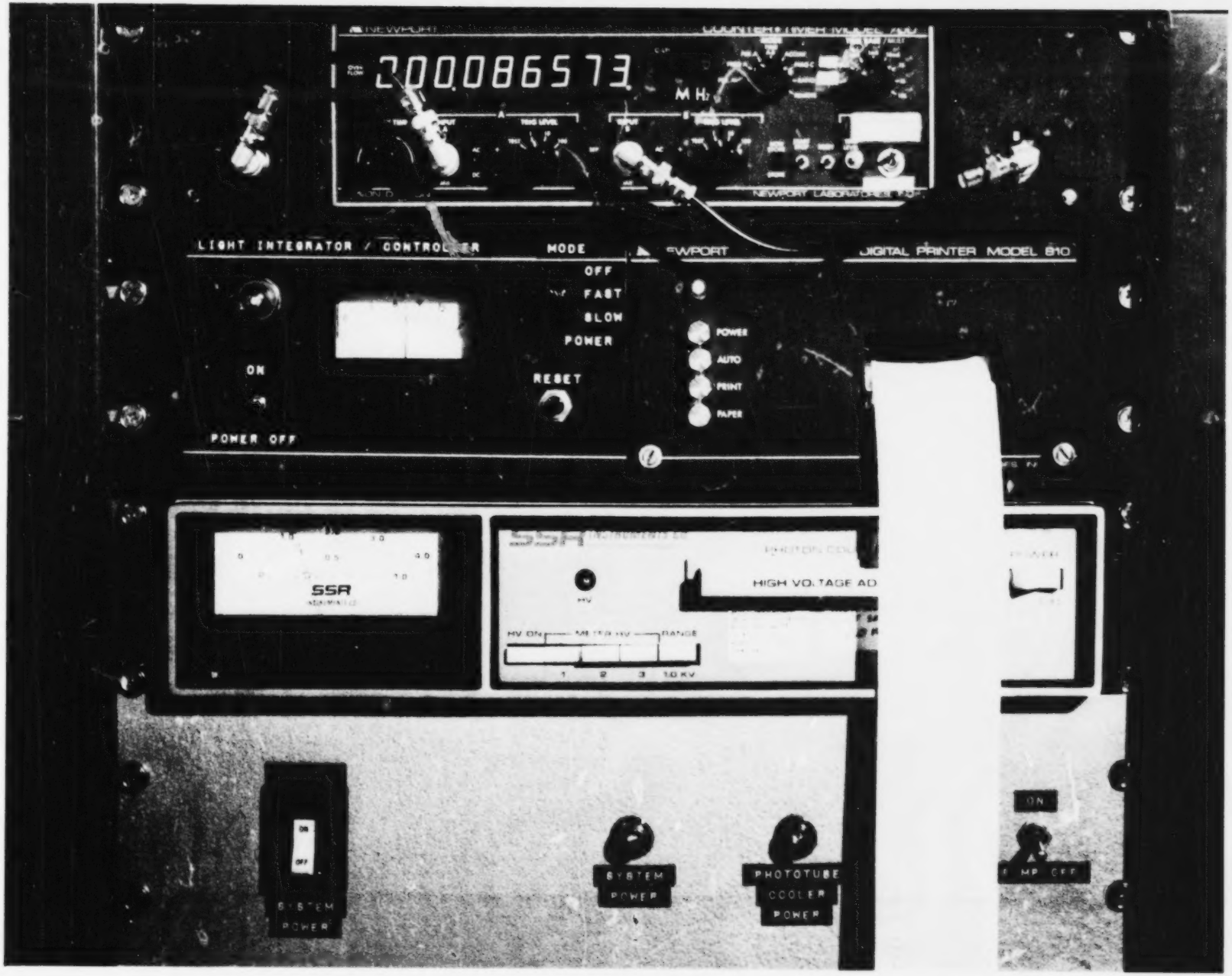


Figure 3, Page 21



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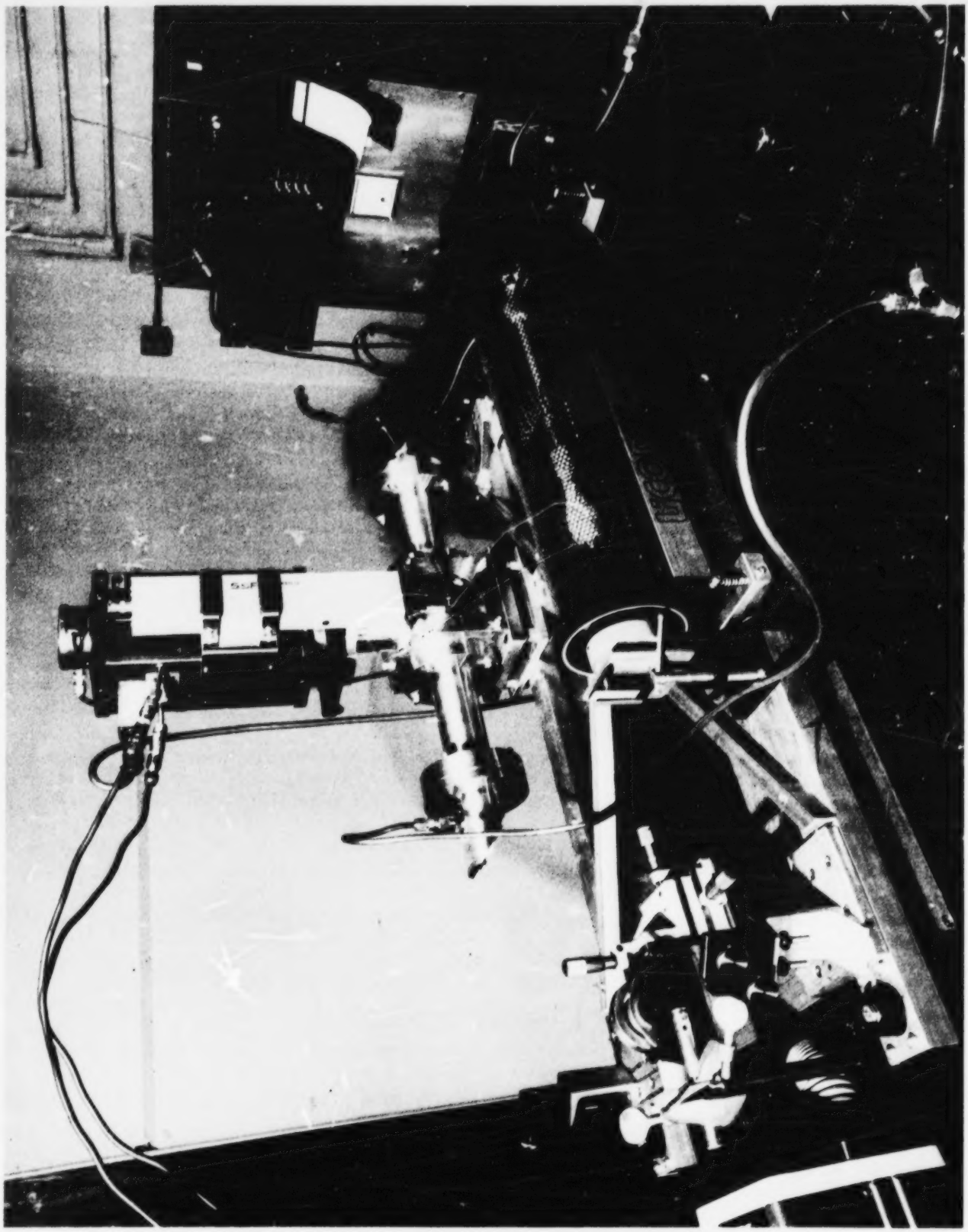

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Optical Subsystem Diagram

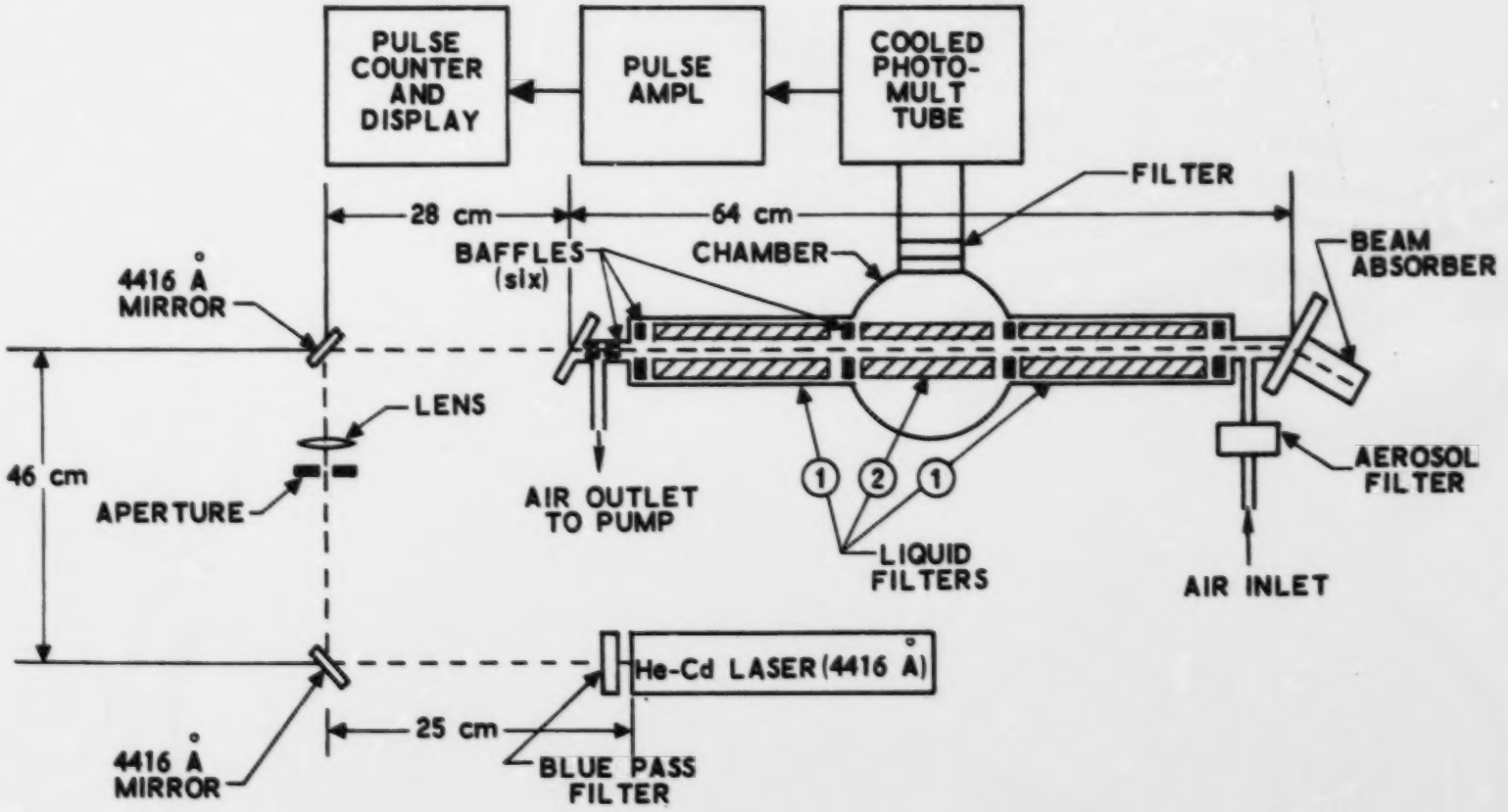

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Figure 6, Page 24

Filter Transmission

$Na_2Cr_2O_7 \cdot 2H_2O$, 304 g/l, 1 cm PATH LENGTH

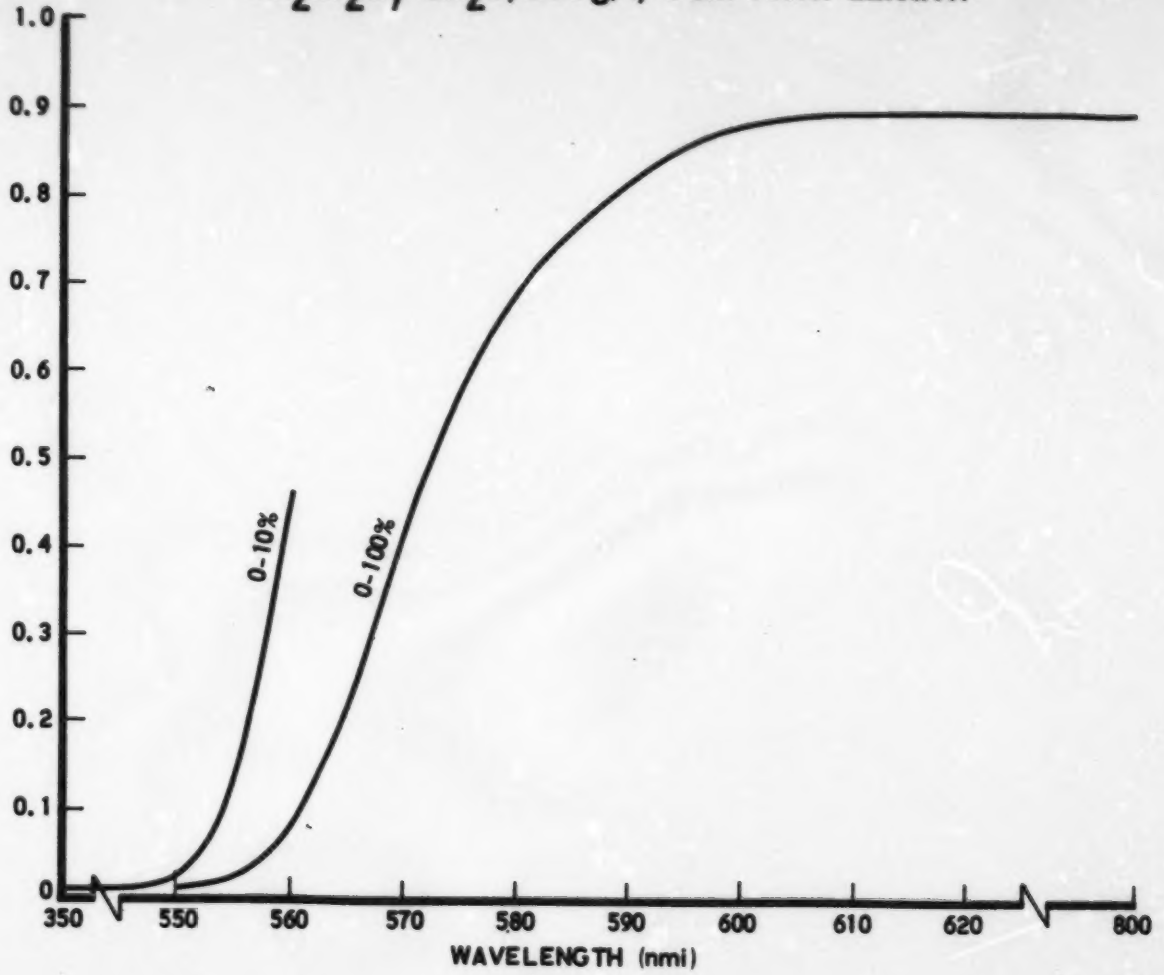
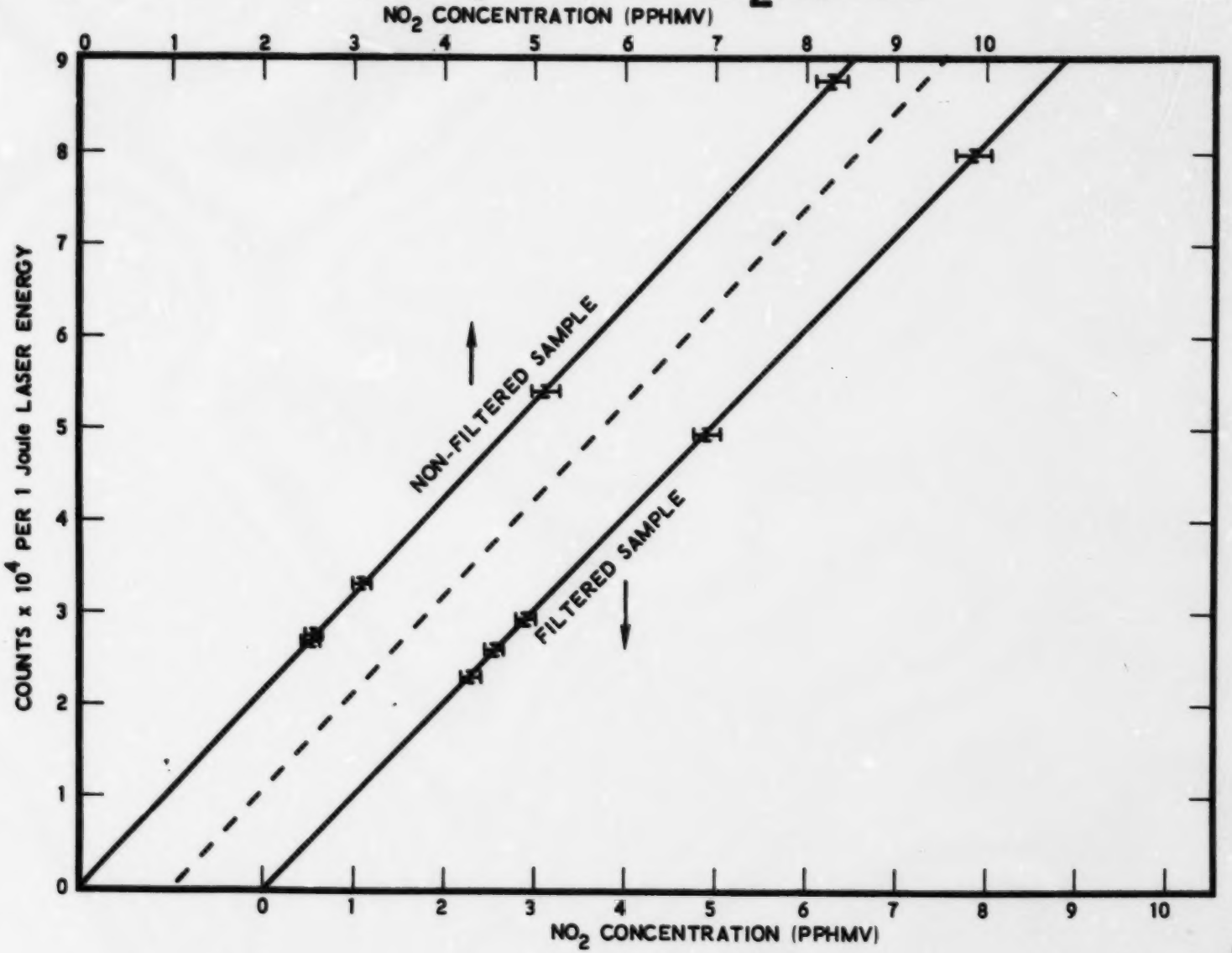


Figure 7, Page 25


Linearity Test for NO_2 Monitor
NO_2 CONCENTRATION (PPHMV)
0 1 2 3 4 5 6 7 8 9 10
COUNTS x 10^4 PER 1 Joule LASER ENERGY
0 1 2 3 4 5 6 7 8 9
NON-FILTERED SAMPLE
FILTERED SAMPLE
0 1 2 3 4 5 6 7 8 9 10
NO_2 CONCENTRATION (PPHMV)

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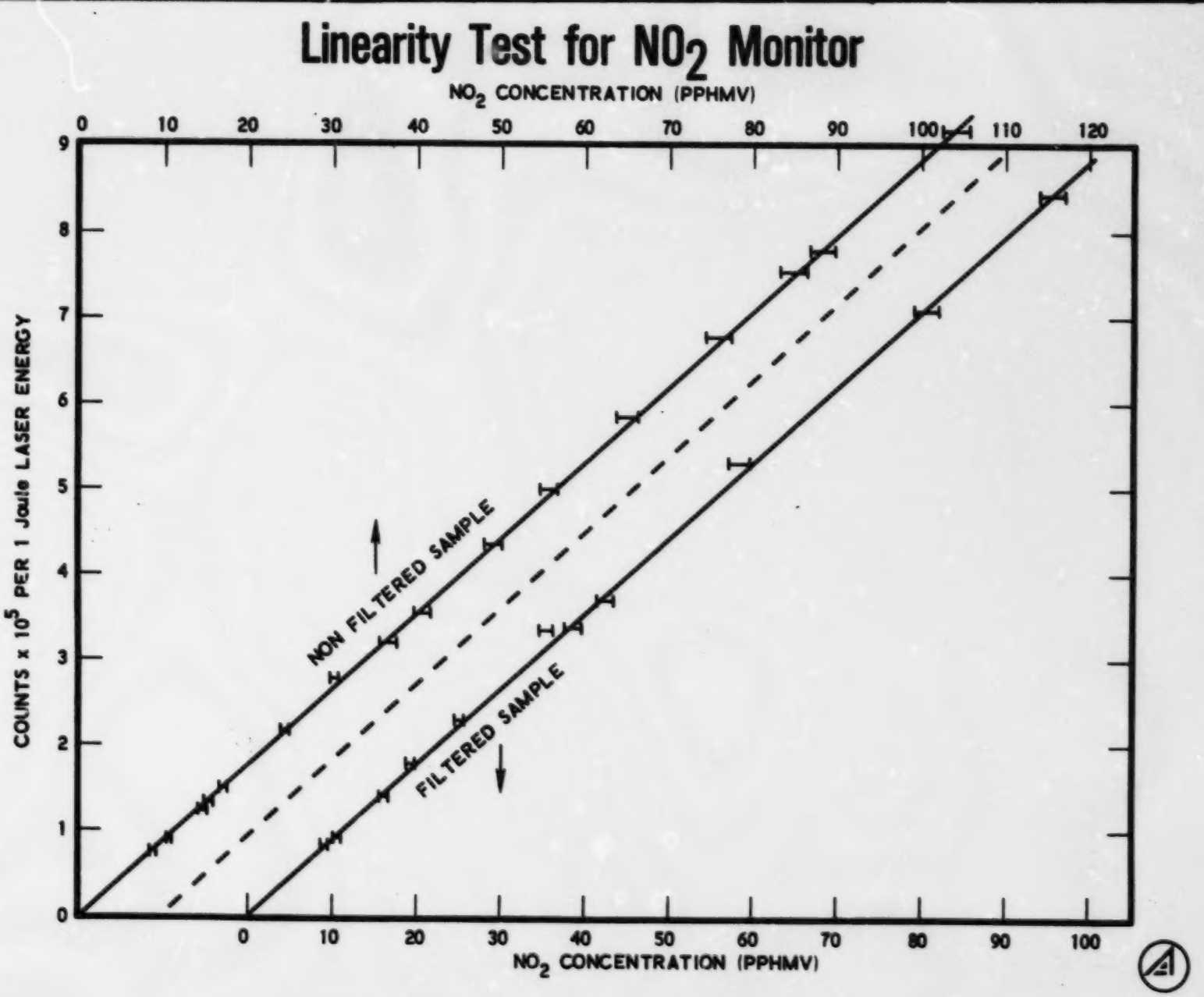
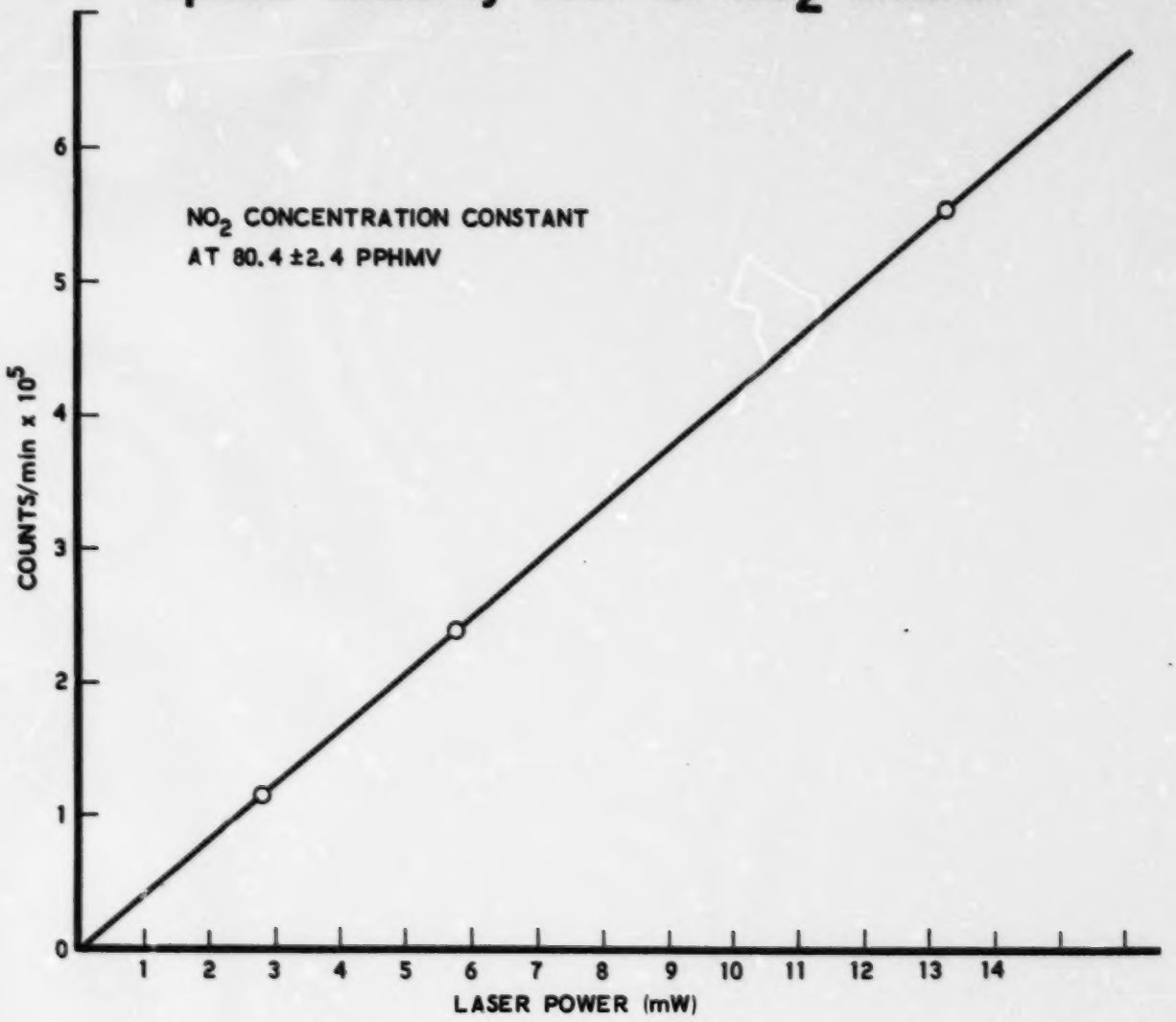

Linearity Test for NO_2 Monitor
NO_2 CONCENTRATION (PPHMV)
0 10 20 30 40 50 60 70 80 90 100 110 120
COUNTS x 10^5 PER 1 Joule LASER ENERGY
0 1 2 3 4 5 6 7 8 9
NON FILTERED SAMPLE
FILTERED SAMPLE
0 10 20 30 40 50 60 70 80 90 100
NO_2 CONCENTRATION (PPHMV)

Figure 9

Optical Linearity Test for NO_2 Monitor



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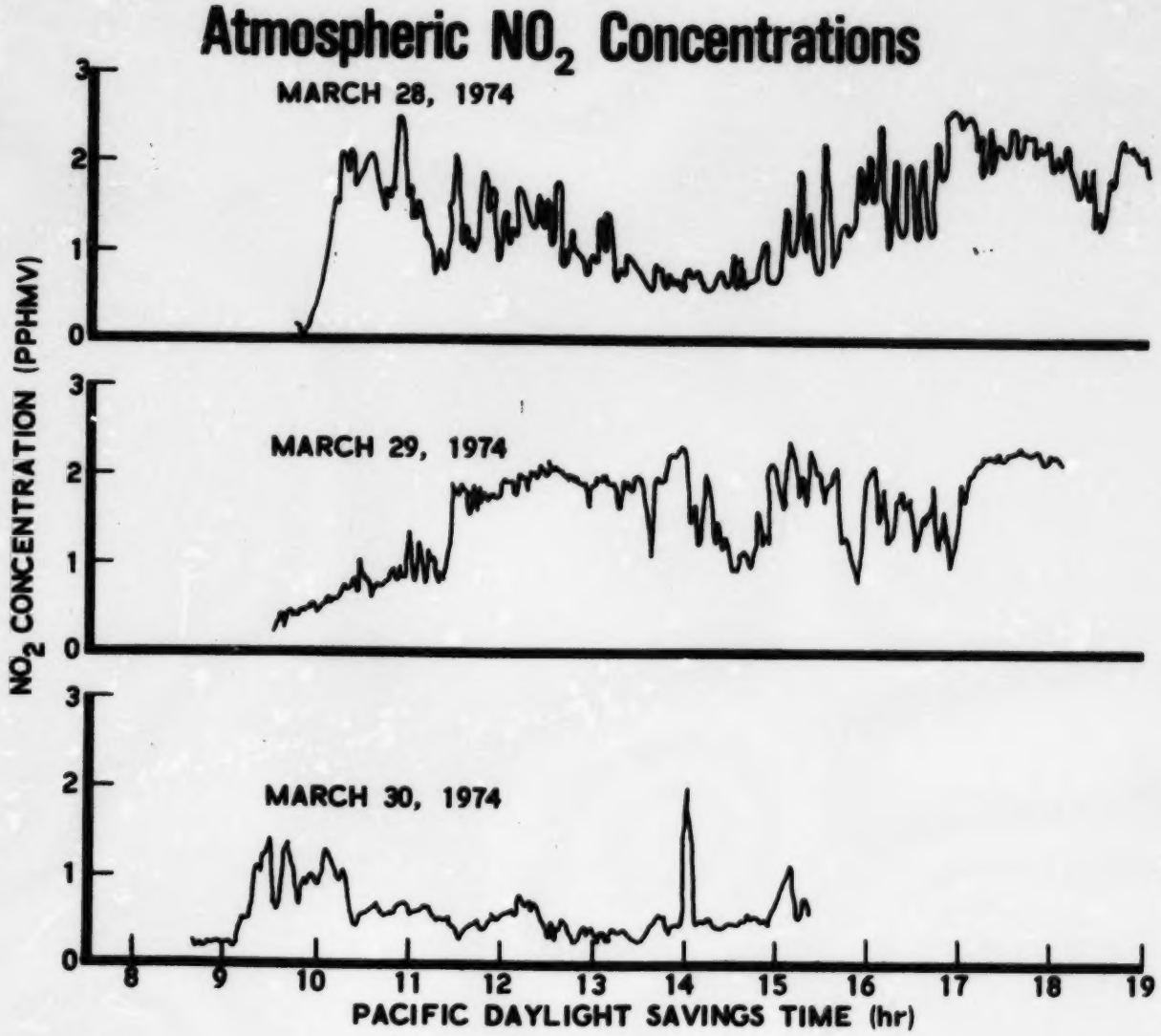

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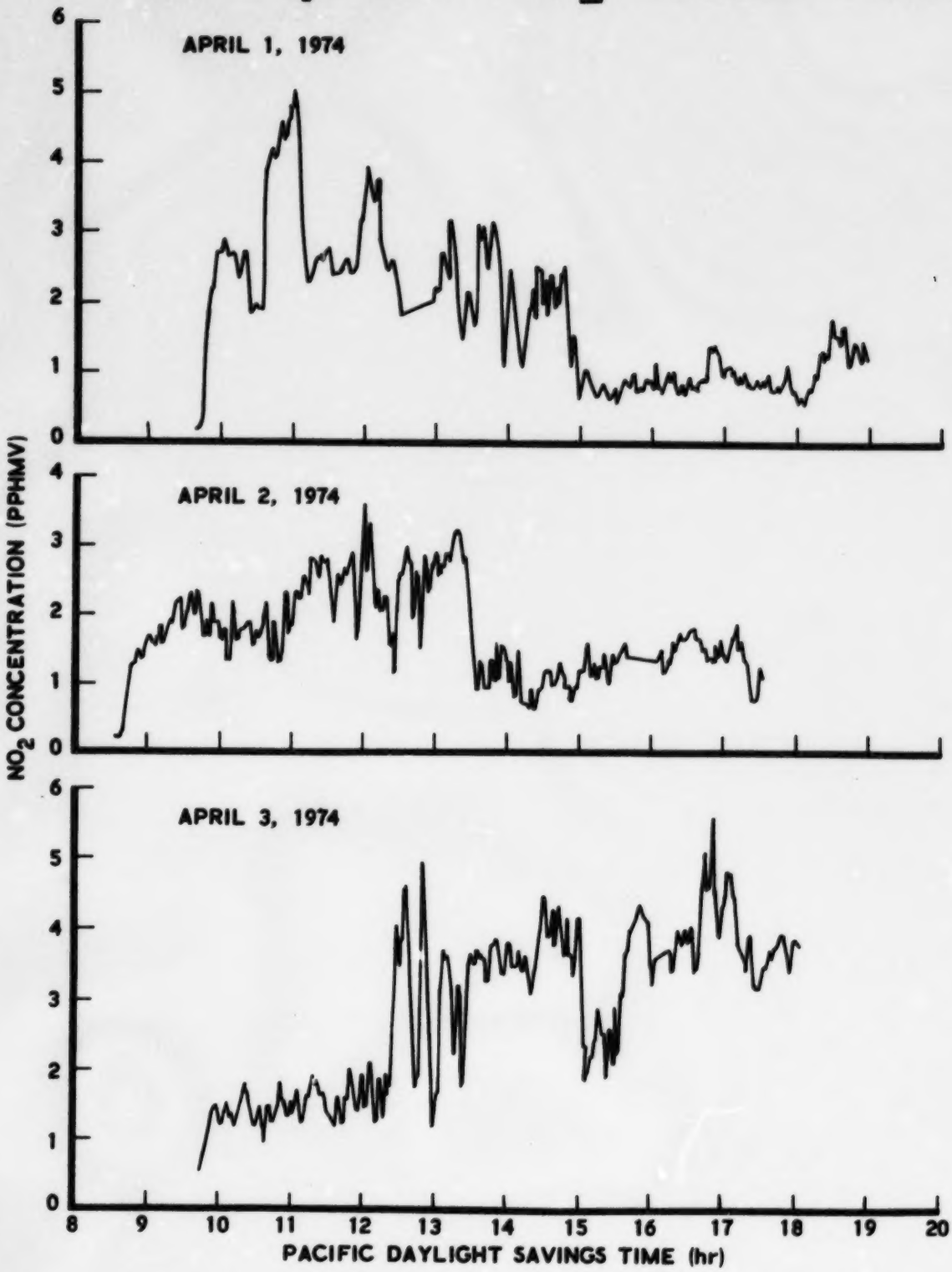
Atmospheric NO_2 Concentrations



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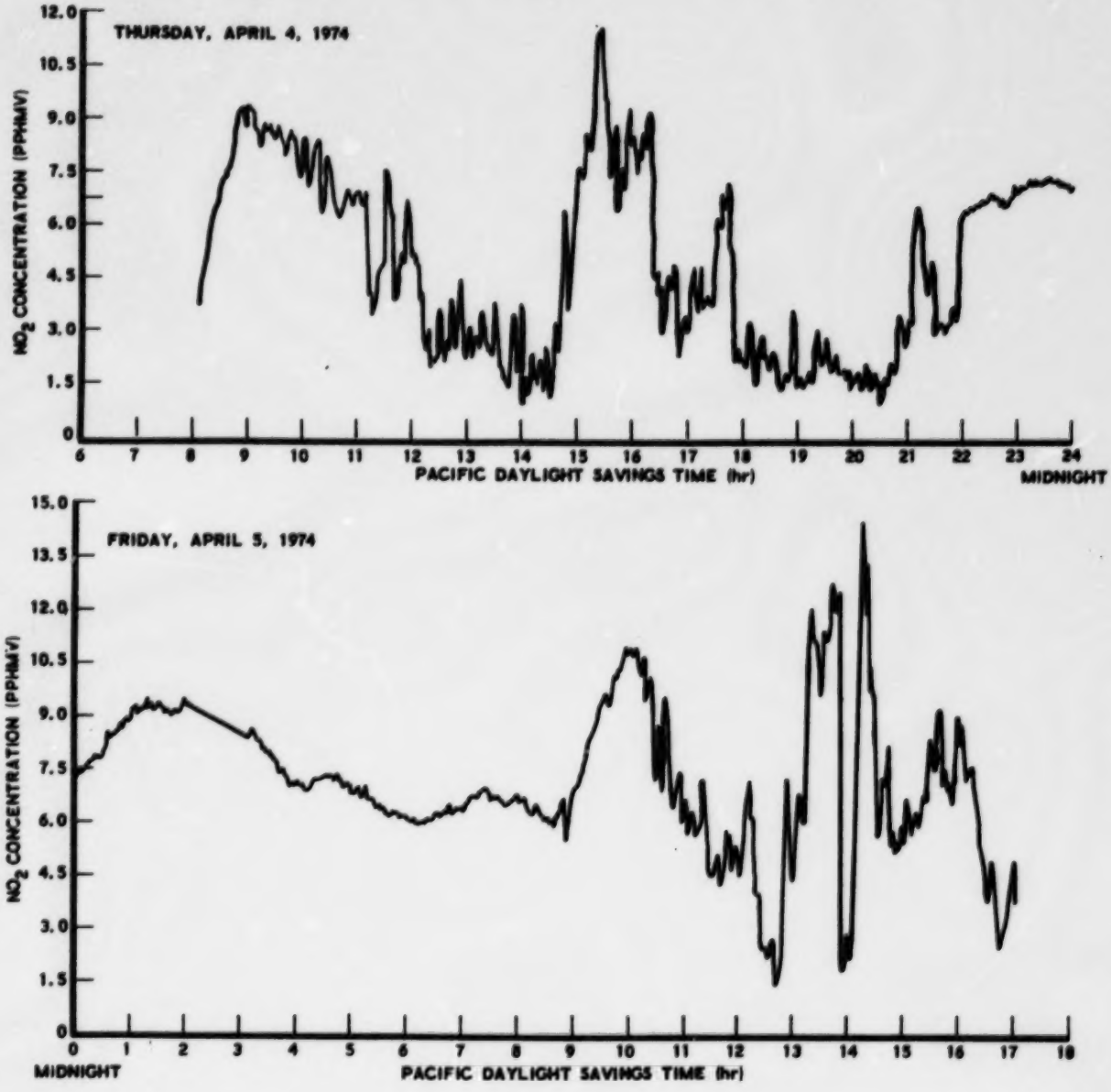
Atmospheric NO_2 Concentrations



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